

NMR Quantum Computation: a Critical Evaluation

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Liquid state nuclear magnetic resonance (NMR) techniques have produced some spectacular successes in the construction of small quantum computers, and NMR is currently by far the leading technology for quantum computation. There are, however, a number of significant problems with any attempt to scale up the technology to produce computers of any useful size. While it is probable that some of these will be successfully sidestepped during the next few years, it is unlikely that they will all be solved; thus current liquid state NMR techniques are unlikely to provide a viable technology for practical quantum computation.

INTRODUCTION

Nuclear Magnetic Resonance (NMR) [1, 2, 3, 4, 5, 6] is almost unique among potential quantum technologies in that it has already been used to build small quantum computers [7, 8, 9, 10, 11]. Although other techniques have been used to implement quantum logic gates, such as the ion trap controlled-NOT gate [12], NMR provided the first complete implementation of a quantum algorithm [10]. Since then progress has been extremely rapid, with demonstrations of Deutsch's algorithm [10, 13], Grover's quantum search [14, 15, 16], versions of the Deutsch-Jozsa algorithm with three [17] and five [18] qubits, and quantum counting [19].

In addition to being one of the most successful quantum computing technologies, liquid state NMR is also among the oldest. Although explicit experimental demonstrations of NMR quantum computation only date from 1996 [7], many "conventional" NMR experiments, such as COSY [20, 21] and INEPT [22] can in retrospect be reinterpreted as quantum computations. These and related experiments, based on coherence transfer sequences, have been in use all over the world for decades, and are regularly used to study complex biomolecules containing thousands of nuclear spins [23]. Even older than these are simpler experiments such as selective population transfer [24], which corresponds to the implementation of a controlled-NOT gate, although in this case the gate was not applied to spins in superposition states.

The rapid progress made in NMR quantum computation builds on this pre-existing experimental sophistication: decades of experience in manipulating nuclear spins in coherent states has inevitably resulted in a wide range of "tricks of the trade". Given this success it may seem surprising that some early papers suggested that this approach might be limited to quantum computers containing about 10 qubits [25, 26], while many more modern estimates are similar at 10–20 qubits. The explanation for this is simple: the highly developed nature of NMR experiments, in comparison with many other putative quantum technologies, means that the limits of the technique are fairly well known and understood. Thus

unduly optimistic predictions about the power of NMR quantum computation may be easily debunked by experienced NMR spectroscopists.

STRUCTURE AND SCOPE

It is conventional when assessing proposals for quantum computation technologies to consider how the technique can be used to implement five basic elements required to build a quantum computer, and then to discuss whether these techniques can be scaled up for use in computers with large numbers of qubits. This approach is not appropriate for NMR, as it is already clear that all the five basic elements can be constructed; indeed they have all been experimentally demonstrated. Thus, the only topic remaining to be addressed is that of scaling. It is, however, useful to consider each of the five basic elements in turn, and discuss their impact upon the practicality of building a large NMR quantum computer.

The sections below are largely concerned with what might be called "conventional" liquid state NMR quantum computers, by which I mean computers implemented using standard techniques from liquid state NMR with spin- $\frac{1}{2}$ nuclei. I will, however, briefly discuss some relatively simple techniques, such as the use of optical pumping or the use of liquid crystal solvents, which may allow small extensions in the range accessible to NMR quantum computers without greatly altering the underlying physics. I will not consider solid-state NMR: although ultimately based on the same physical interactions the solid state NMR Hamiltonian [27, 28, 29] is *much* more complicated than the liquid state form, and liquid and solid state NMR form two largely separate sub-fields. While some solid state NMR experiments could be considered as implementations of quantum simulations (*e.g.*, [30]), they have not as yet been used to build general purpose quantum computers. Similarly, while nuclei with spin quantum numbers greater than $\frac{1}{2}$ (quadrupolar nuclei) are of some theoretical interest [31, 32], their use raises considerable experimental difficulties. Finally I will largely ignore proposed systems which use single isolated atomic nuclei in solid state devices, such as the proposal due

to Kane [33, 34]; although such systems are ultimately based upon NMR, they differ from current liquid state NMR implementations so profoundly that it is difficult to draw detailed parallels.

INITIALIZATION

Initialization is the process of placing a quantum computer in some well defined initial state, typically $|0\rangle = |000\dots 0\rangle$, prior to beginning the computation. In principle any initial state is as good as any other, but in practice $|0\rangle$ is the most widely chosen, both because it corresponds to the traditional starting point of many quantum algorithms and because it often corresponds to the system's energetic ground state. This is indeed the case in NMR quantum computation, where the computational basis corresponds with the natural experimental basis.

As initialization requires that the quantum computer be placed in the state $|0\rangle$, independent of its state before the beginning of the initialization process, it is clear that it cannot be achieved by any unitary process; thus initialization schemes must be quite different from quantum logic gates. As the desired initial state is usually an energetic ground state, initialization is typically achieved by cooling. This is not a practical approach within NMR, as the energy gaps involved are tiny compared with the Boltzmann factor at room temperature.

The energy gap between nuclear spin levels in NMR experiments is principally determined by the Zeeman interaction between the nucleus and the applied magnetic field (with the exception of the quadrupolar interaction, which does not occur in spin- $\frac{1}{2}$ nuclei, all other nuclear spin interactions are small compared with the main Zeeman interaction). The Zeeman splitting, $\Delta E = h\nu = \hbar\gamma B$, is usually described in terms of the corresponding Larmor frequency, ν , and is proportional to the magnetic field strength, B , and the gyromagnetic ratio, γ , which is an intrinsic property of the nucleus. For the magnetic field strengths typically used in NMR experiments (2.3–21.1 T), the Larmor frequency of ^1H nuclei lies in the range 100–900 MHz, corresponding to an energy of 0.4–3.7 μeV . For all other nuclei (with the exception of the radioactive nucleus tritium, ^3H), γ is lower than for ^1H , with a corresponding reduction in ΔE .

These energies are much smaller than the Boltzmann energy at room temperature (about 25 meV), and so at thermal equilibrium the excess population in the lower Zeeman level is tiny, less than one part in 10^4 . For this reason conventional liquid state NMR was long ruled out as a practical technology for quantum computation. In 1996, however, it was realised that it is not strictly necessary to start quantum computations from a pure state: a pseudo-pure, or effective pure state will suffice [7].

Pseudo-pure states

A pseudo-pure state is a mixed quantum state corresponding to a mixture of the desired quantum state, $|\psi\rangle$ and the maximally mixed state, $\mathbf{1}/N$, where $N = 2^n$ is the dimension of the Hilbert space describing the system. To perform a quantum computation it suffices to form the pseudo-pure ground state,

$$\rho = (1 - \epsilon)\mathbf{1}/N + \epsilon|0\rangle\langle 0|. \quad (1)$$

An otherwise error-free quantum computer which begins a computation in such a state will end up in the state

$$\rho' = (1 - \epsilon)\mathbf{1}/N + \epsilon|\psi\rangle\langle\psi| \quad (2)$$

where $|\psi\rangle$ is the result of the computation (assumed for the moment to be an eigenstate in the natural basis). This result may be immediately deduced by noting that any quantum computation corresponds to some unitary evolution of the quantum state; such evolutions are linear and have no effect upon $\mathbf{1}$.

A quantum computer in this mixed state will return the correct answer with probability $\epsilon + (1 - \epsilon)/N$, and a wrong answer with probability $(N - 1)(1 - \epsilon)/N$ (note that the maximally mixed state itself contains a fraction $1/N$ corresponding to the ground state). Clearly it is possible to determine the desired answer by statistical analysis of the results of a sufficiently large number of repetitions of the computation, where the number of repetitions required depends on ϵ . Equivalently it is possible to use an ensemble of quantum computers, and determine the ensemble averaged result of the computation; as long as the ensemble is sufficiently large this process will unambiguously point to the desired answer.

This latter approach is precisely that adopted for NMR quantum computation, and indeed for conventional NMR spectroscopy. NMR transition frequencies are so low that it is essentially impossible to detect a single transition, and so it is necessary to use macroscopic samples, typically containing about 10^{17} molecules, with an excess population of about 10^{13} nuclei in the low energy state. It might seem that the small signal from the excess population would be swamped by a huge background, but this is not the case as the maximally mixed state gives rise to no overall signal. This is because the signals from different components in the maximally mixed state cancel each other out; the operators corresponding to the effective observables in NMR spectra are all traceless. Thus the NMR signal arises entirely from the small excess population, and the signal from an NMR quantum computer in the pseudo pure state, equation (2), is identical to that from one in the pure state $|\psi\rangle\langle\psi|$, except that the signal strength is reduced by a factor of ϵ .

Assembling pseudo-pure states

While pseudo-pure states offer the theoretical possibility of performing quantum computations with mixed states, this approach is useful only if some practical procedure for assembling such states can be devised. For the simplest possible quantum computer, comprising a single qubit, the process is trivial, as the thermal equilibrium density matrix has exactly the desired form, but with larger systems the situation is more complicated. For a system of n spin- $\frac{1}{2}$ nuclei, all of the same nuclear species (a homonuclear spin system), the 2^n eigenstates will be distributed across an evenly spaced ladder of $n+1$ groups of energy levels, with the number of (nearly degenerate) states within each group given by Pascal's triangle; the population of each state will be determined by the Boltzmann equation. If the system contains several different nuclear species (a heteronuclear system), the situation is similar but slightly more complicated. Normally NMR experiments are conducted in the high temperature limit (see below), and so the pattern of excess populations will simply be proportional to the energy of each state.

Assembling a pseudo-pure state from such a complex mixture might seem difficult, but it is in fact a fairly conventional problem from the viewpoint of NMR [7]. The apparent problem is that reaching even a pseudo-pure state requires a non-unitary process, and the most obvious such process (relaxation to thermal equilibrium) leads to a state which is neither the desired state, nor unitarily related to it. Thus some additional non-unitary step is required.

In fact there are two elements commonly used in NMR pulse sequences with non-unitary effects: magnetic field gradients and phase cycling. The first of these relies on the fact that the sample forms a macroscopic ensemble; by applying Hamiltonians which vary over the sample the *ensemble averaged* evolution can be non-unitary. This is most commonly achieved by momentarily destroying the spatial homogeneity of the main magnetic field (a B_0 field gradient pulse [35]), but similar effects can be achieved using spatially inhomogeneous RF fields (a B_1 field gradient pulse [36]). The second approach relies on combining the results of several subtly different NMR experiments by post-processing; as this is done by classical methods, such processing is not confined to unitary transformations. In conventional NMR this is referred to as phase cycling [37], and plays a central role in many experiments, although for many purposes it has now been replaced by the use of gradient techniques.

Both of these approaches have been used to assemble pseudo-pure states. The original approach of Cory *et al.* [7], based on magnetic field gradients, is in many ways the most satisfying, but an alternative “temporal averaging” scheme based on phase cycling [38] has also proved extremely popular. Recently Knill *et al.* have described

a simple and general approach [39] for building pseudo-pure states in a system of any size; their scheme may be used with either gradient or phase cycling techniques.

In addition to these schemes, another quite different approach, logical labeling, was suggested very early on by Gershenfeld and Chuang [9]. Their approach is based on the observation that while the thermal equilibrium spin density matrix for an n spin system ($n > 1$) does not have the desired form, equation (1), subsets of energy levels can be chosen which *do* have the correct pattern of populations; the computation is then performed within this subset of states. Although theoretically elegant this scheme appears to be more complex than the other approaches, and only two experimental implementations have been reported [40, 41].

Scaling the system up

While pseudo-pure states provide a practical approach for building small NMR quantum computers it is not possible to simply scale this approach up to larger systems. The basic problem is the size of ϵ , or rather the manner in which ϵ scales with n , the number of spins in the system.

The exact value of ϵ will vary with details of the scheme used to prepare the pseudo-pure state, and so it is more useful to consider an upper bound, which gives the maximum amount of pseudo-pure state which can possibly be extracted from thermal equilibrium. This is equal to the population difference between the lowest and highest energy states [25], which for an n spin homonuclear spin system is given by

$$\epsilon = \frac{2 \sinh(nh\nu/2kT)}{2^n \cosh^n(h\nu/2kT)} \quad (3)$$

where $h\nu$ is the Zeeman splitting. In the high temperature limit ($h\nu \ll kT$) this expression simplifies to

$$\epsilon \approx \frac{nh\nu/kT}{2^n}. \quad (4)$$

Thus, in the high temperature limit the amount of pseudo-pure state which can be obtained decreases *exponentially* with the size of the spin system. To overcome this it is necessary to use an exponentially large sample, or some equivalent approach such as repeating the experiment an exponentially large number of times. It therefore seems that the pseudo-pure state approach does not scale.

In passing it should be noted that this is by no means a feature unique to NMR quantum computation: it occurs for any ensemble quantum computation scheme in the high temperature limit. Physically this is because such a system has 2^n levels, and the population deviations must be distributed among them; hence the excess population in any one state is inevitably exponentially small.

The exponentially small size of ϵ has caused some authors to dismiss NMR quantum computation as a practical approach; while this point of view has merit it may, as discussed below, be over hasty. More recently, it has been suggested [42] that NMR might not be quantum mechanical at all! As NMR experiments are conducted in the high temperature limit, the density matrix is close to a maximally mixed state, and such high temperature states can always be decomposed as a mixture of product states (that is, states containing no entanglement between different nuclei). As NMR states can be described without invoking entanglement, they can therefore be modeled classically, although the classical models involved may be somewhat contrived. While this conclusion is clearly correct it has proved difficult to develop classical models which fully describe NMR experiments [43], and the real significance of these observations remains unclear.

High fields and low temperatures

As the problem with using pseudo-pure states arises from operating in the high temperature limit, the most obvious solution is to use either low temperatures or high fields, so that this limit no longer applies. Unfortunately NMR lies so far into the high temperature regime that this approach is unlikely to lead to success.

The critical fields and temperatures required are given by $\hbar\gamma B \sim kT$; for ^1H nuclei and a magnetic field strength of 21.1 T (the largest NMR magnet currently available) this corresponds to $T \sim 0.043$ K. Reaching such temperatures is possible, but clearly the sample will no longer remain in the liquid state! At such low temperatures only solid state NMR is possible. Alternatively if the sample is held at room temperature then a magnet with a field strength $B \sim 150000$ T will be required; this lies far beyond anything which is likely to be achieved in the foreseeable future.

The arguments above do not entirely rule out the possibility that some combination of high fields and low temperatures might one day be used to achieve reasonable polarizations, and thus interesting pseudo-pure states (in particular, it may be possible to generate high polarizations under one set of conditions and then observe them in another), but in the short term this does not seem a particularly sensible approach. There are, however, a wide range of alternatives.

Optical pumping

A more subtle approach to increasing spin polarization is to use techniques such as optical pumping; this has the effect of decreasing the apparent temperature of the spin system without affecting the rest of the sample. Optical pumping techniques are in fact quite widely used within

NMR, but it is not yet clear whether they can be usefully applied within NMR quantum computation.

The best known optical pumping process within NMR is the spin-exchange optical pumping of noble gas nuclei [44], most notably the spin- $\frac{1}{2}$ nuclei ^3He and ^{129}Xe and the quadrupolar nucleus ^{131}Xe . The process involves conventional optical pumping of the electron spin states of alkali metal atoms, followed by spin exchange in binary collision pairs (He) or van der Waals complexes (Xe). The resulting highly polarized noble gases have been used in a variety of NMR experiments, including NMR imaging [45]. Unfortunately noble gases are unsuitable for constructing NMR quantum computers as they consist of isolated atoms, that is systems containing only a single spin. It is in principle possible to transfer the polarization from the noble gas to more interesting species using a variety of cross polarization techniques [46, 47, 48], although it has so far proved difficult to obtain high transfer efficiency except when transferring polarization to surface species in microporous materials.

The second common form of optical pumping in NMR is quite different: optical pumping in bulk semiconductors such as Si, GaAs and InP [49]. This approach, which is related to the DNP schemes described below, is confined to solid state systems, and it is difficult to see how it might be used to improve current liquid state implementations of NMR quantum computers.

Other approaches

There are many other techniques which can be used to increase the initial polarization in NMR experiments: the low sensitivity of NMR is perhaps its biggest drawback in conventional spectroscopic studies, and seeking to improve sensitivity is a common research topic.

Perhaps the most important technique for sensitivity enhancement is the nuclear Overhauser effect (NOE), which arises from the correlated relaxation of two or more nuclei. If the polarization of one nucleus is perturbed from its equilibrium value cross relaxation will transfer some of this perturbation to other nearby nuclei. This technique is widely used, both to enhance the polarization of low sensitivity nuclei, and to probe internuclear distances [50]. The maximum polarization gain which can be achieved, however, is proportional to γ_S/γ_I , where γ_S and γ_I are the gyromagnetic ratios of the sensitive and insensitive nuclei respectively, and so this method cannot be used to increase the polarization of ^1H , which has the highest gyromagnetic ratio among stable nuclei.

A better approach for ^1H nuclei is to use the original Overhauser effect [51, 52], which transfers polarization from electrons to nuclei. Initially greeted with scepticism [53], Overhauser's theoretical predictions were confirmed by Carver and Slichter [54], who demonstrated huge Overhauser enhancements in the spectrum of metallic

⁷Li. The Overhauser effect, and related phenomena collectively known as Dynamic Nuclear Polarization or DNP [55, 56, 57], can be used to generate quite large polarization enhancements in a range of solid systems containing unpaired electrons, and when combined with optical techniques for pumping the electron polarization [49, 58] dramatic enhancements can be observed [59]. However the technique performs poorly in the liquid state.

Another technique which gives enhanced polarizations is Chemically Induced Dynamic Nuclear Polarization, or CIDNP [60]. Despite the name CIDNP is unrelated to DNP; instead the non-equilibrium polarizations arise from a spin sorting mechanism which takes place during chemical reactions. This intriguing effect has proved a powerful tool for investigating a range of biomolecular systems [60, 61], but the polarizations achievable are unlikely to be useful for quantum computation.

Yet another possible approach is a family of experiments using *para*-hydrogen induced polarization, or PHIP [62]. When hydrogen molecules are cooled into their rotational ground state, the Pauli principle dictates that the nuclear spin wavefunction of the two ¹H nuclei must be antisymmetric, and so the two nuclei must have *opposite* spin states. If *para*-hydrogen is used in an addition reaction, for example adding H₂ across a carbon-carbon double bond, then the product of the reaction will also have non-equilibrium spin states; these can be converted into a greatly enhanced polarization by conventional NMR pulse sequences. As *para*-hydrogen has a pure nuclear spin state it should in principle be possible to produce completely polarized molecules; in practice the enhancements are usually somewhat smaller [62].

Unlike many of the schemes discussed above, PHIP works well in the liquid state using fairly “normal” organic molecules, and so may prove useful in NMR quantum computation. Unfortunately the scheme only allows the production of molecules which are highly polarized at two sites, and while it is in principle possible to use two or more addition reactions within the same molecule to produce polarization at four or more sites creating an entire spin system by PHIP addition reactions does not seem a plausible process. However, as discussed below, in some cases it may suffice to produce high polarizations at a single spin; in this case PHIP may indeed turn out to be a useful approach.

Reinitialization

One important point, frequently neglected in discussions of this kind, is that the methods described above are essentially methods for initializing an entire quantum computer at the start of a computation. They do not obviously permit the selective reinitialization of individual qubits in the middle of a computation. This makes it difficult to implement effective error correction schemes,

as discussed in section below.

Computational solutions

In addition to the physical approaches outlined above, two computational approaches might allow the problem of low spin polarization to be bypassed.

The first approach, due to Schulman and Vazirani [63], uses computational methods to purify mixed states. Their scheme works by concentrating the polarization from a large number of weakly polarized spins into a small number of spins which become strongly polarized; alternatively the calculation can be thought of as occurring inside a small effectively pure subspace within the large spin space. Unfortunately the size of the subspace which may be extracted is $O(\epsilon^2 n)$, and so an n spin quantum computer requires a spin system with $O(n/\epsilon^2)$ spins; for the values of ϵ achievable by direct cooling the resulting overhead is enormous. If, however, the polarization can be substantially increased by other means then this might provide a good method for further purification.

Another recent theoretical discovery may allow all these problems to be sidestepped, as it may be possible to perform many important quantum computations without starting from a pure (or even pseudo-pure) ground state. It has been known for some time that some quantum computations can be performed with a starting state comprising one pure qubit together with a number of qubits in the maximally mixed state [64]; more recently it has been shown that Shor’s quantum factoring algorithm can be performed in this way [65] (but see section below). If this proves to be a useful approach then it could simplify the problem of constructing an NMR quantum computer, as single qubit pure states may be substantially easier to reach than their multi qubit equivalents (for example, by using *para*-hydrogen based schemes).

GATES

In comparison with initialization, building quantum gates is a relatively simple process for NMR quantum computers. Indeed, as described above, many conventional NMR pulse sequences used in the molecular sciences can be viewed as sequences of quantum gates.

Any quantum gate can be built out of one qubit and two qubit gates [66], and early work concentrated on building these gates in two qubit NMR quantum computers (NMR systems containing two spins). Unlike many other proposed implementations of quantum computation, these gates cannot simply be transferred to larger spin systems without modification, and there was some initial concern that this transfer might prove difficult, involving an exponential increase in the complexity of the gate design. In fact, while the gates do need to be

modified, the transfer can be done fairly simply, and approaches are known for doing this with only quadratic overhead. More recently some authors have moved on from simply imitating gates used in “conventional” quantum computers, and started designing gates which harness the full power of the NMR Hamiltonian directly.

One qubit gates

One qubit gates are easy to implement in NMR as they correspond to rotations of a single spin within its own subspace. This is most simply described using the Bloch vector model [5, 67] in which the state of a spin (or indeed any qubit) is represented by a point on the surface of the Bloch sphere. One qubit gates correspond to rotations on this sphere, and can be achieved using resonant radiofrequency (RF) fields; the power and length of the RF pulse determines the rotation angle, while the phase of the RF radiation corresponds with the rotation axis within the xy plane. Rotations around other axes can be achieved by composite rotations, implemented by applying several RF pulses in sequence [6].

This description assumes that it is possible to apply RF pulses selectively to individual qubits. In more conventional proposals for implementing quantum computation such qubit selection is achieved using spatial localisation: each qubit is stored on some physical object with a well defined location. This approach is not possible within NMR for three reasons. Firstly, each qubit is not stored on a single spin, but rather in an ensemble of spins distributed throughout the sample. Secondly, as the sample is in the liquid state individual spins are in continual rapid motion. Thirdly, the wavelength of RF radiation (around 1 metre) is huge compared with the separation between spins, rendering conventional spatial localisation impossible (although this could in principle be overcome by using techniques from magnetic resonance imaging (MRI) combined with enormous field gradients [68, 69]).

Instead of using spatial selection, NMR quantum computation relies on frequency selection to pick out individual qubits. Different nuclear species have different gyromagnetic ratios, and thus different resonance frequencies; therefore RF pulses on resonance with one spin will have little or no effect on other spins. With two or more nuclei of the same type the situation is slightly more complex, but even these will have different resonance frequencies as different chemical environments will result in different chemical shift (shielding) interactions [5]. In this case it is necessary to use low power selective RF pulses (“soft” pulses) [6], or their multipulse equivalents, Dante sequences [70], in order to excite one spin while leaving other spins with only slightly different resonance frequencies untouched (the excitation bandwidth of an RF pulse depends on its power). This approach works well in small spin systems, but will be difficult in large systems as dis-

cussed below.

Two qubit gates

Two qubit gates are slightly more complex, as they require some sort of interaction between pairs of spins. In liquid state NMR quantum computers this is provided by scalar spin–spin coupling [5]. The NMR Hamiltonian describing two weakly coupled spins is

$$\mathcal{H} = \omega_I I_z + \omega_S S_z + \pi J_{IS} 2I_z S_z \quad (5)$$

where, following NMR practice, the spin operators are described using product operators [71, 72], and energies are written as multiples of \hbar . The one spin angular momentum operators I_z and S_z are simply scaled versions of the Pauli matrices (the use of I and S to describe two spin systems is traditional [73]); ω_I and ω_S are the resonance frequencies (Larmor frequencies) of the two spins, and J_{IS} is the scalar spin–spin coupling (J-coupling), usually measured in Hertz. Note that this simplified Hamiltonian is only correct in the *weak coupling limit*, that is when $|2\pi J| \ll |\omega_I - \omega_S|$.

The most obvious way to implement a two qubit gate, such as the controlled-NOT gate, is to use soft pulse techniques to selectively excite one spin only when its neighbouring spin is in one of its two eigenstates [74]; these two transitions have different energies as they are split by spin–spin coupling. This direct approach, picking out one transition from the multiplet corresponding to transitions of a single spin, is in fact identical to the old selective population transfer experiment [24], and so this is the oldest method for building quantum logic gates. More recently this approach has been used to build two and three qubit gates directly [17, 41, 75].

This direct approach is, however, relatively unpopular. Instead, most authors [7, 8, 9, 10, 13, 14, 15, 16, 18, 19, 40, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90] prefer to use multipulse NMR techniques [1, 2, 3, 4, 6] to sculpt the Hamiltonian, equation (5), into a more suitable form. This is analogous to the replacement of selective population transfer by the INEPT pulse sequence [22]. The basic idea behind Hamiltonian sculpting is to use spin echoes [6, 91, 92] to refocus specific interactions in the Hamiltonian, thus creating an effective Hamiltonian obtained by rescaling elements of the original Hamiltonian, or indeed completely deleting them. While this approach to implementing two qubit gates can be described in a variety of different ways, they are all fundamentally equivalent. The central feature is the implementation of a controlled phase gate [81], such as

$$\phi = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & e^{i\phi} \end{pmatrix}. \quad (6)$$

This can be decomposed in product operator notation as

$$\phi = \exp \left[-i \times \frac{1}{2} \phi \times \left(-\left(\frac{1}{2}E\right) + I_z + S_z - 2I_z S_z \right) \right]. \quad (7)$$

The first term ($\frac{1}{2}E$) can be ignored as it simply corresponds to an (undetectable) global phase; the remaining three terms can be achieved by sculpting the Hamiltonian, equation (5), into the desired form.

More recently a third approach for implementing two qubit gates has been suggested [93]. Once again this method relies on the use of controlled phase gates, but the phase shifts are generated not by using conventional dynamic phases, but instead by geometric phases [94], such as Berry’s phase [95]. Berry phases have been demonstrated in a wide variety of systems [94], including NMR [96, 97] and the closely related technique of NQR [98, 99, 100, 101]. They can be used to implement controlled phase shift gates in NMR systems [93], but it seems that this approach has few advantages for NMR quantum computation over the more conventional dynamic approach; the idea may, however, prove useful in other systems [102].

Gate times

It is not sufficient simply to show that a gate can in principle be implemented; it is also important to consider how long it takes to implement it. As discussed in section below, what matters is not the absolute time taken, but how this compares with the natural decoherence time. It is, therefore, important to consider what factors limit the rate at which NMR quantum, logic gates operate.

One qubit gates are not only simple to build, they are also rapid to operate. As single qubit gates correspond to rotations, a reasonable measure is provided by the inverse of the time required to perform a 2π rotation. For a fully heteronuclear spin system (that is, a spin system containing only one spin of any given nuclear species) this rate is limited only by the available RF power and the breakdown voltages of the RF coils; typical values lie in the range 10–100 kHz. For a homonuclear spin system the situation is more complex as it is necessary to use selective excitation. In this case the gate rate is constrained by the frequency difference between the resonances which must be excited and those which must be left untouched. This can be seen either by considering a Fourier spectral model of excitation [1], or by analysis of the “jump and return” pulse sequence [103]. Thus in homonuclear spin systems the one qubit gate rate is often below 1000 Hz.

Two qubit gates are typically much slower. If they are implemented by direct selective excitation, then the situation is the same as for one qubit gates in homonuclear systems, except that the relevant frequency splitting is the scalar coupling between the spins, J_{IS} . A similar argument applies if the gates are implemented using multiple pulse techniques: the relevant rate is the inverse of

the time required to achieve the “antiphase” condition, $1/2J_{IS}$. Scalar couplings are quite variable, but they are frequently less than 10 Hz; thus the gate times required for two qubit gates can be quite long. In our two qubit NMR quantum computer based on cytosine, a two qubit gate takes about 70 ms. If implemented using geometric phases [93], the time required is even greater.

In order to reduce these two qubit gate times it is necessary to increase the size of the spin–spin coupling constant. In general this is not possible, as J_{IS} is fixed by the chemical system chosen (it is, of course, possible to choose a new system with a larger coupling constant, but this approach is obviously quite limited). It is, however, possible to change the apparent size of J_{IS} by partially reintroducing dipolar couplings. The scalar coupling is in fact a quite small effect in comparison with the principal spin–spin coupling interaction, dipolar coupling. This arises from the direct magnetic interaction between two magnetic dipoles, and in the high field approximation [1]

$$\mathcal{H}_D = \frac{\mu_0 \gamma_I \gamma_S \hbar (1 - 3 \cos^2 \theta)}{8\pi r^3} (3I_z S_z - \mathbf{I} \cdot \mathbf{S}), \quad (8)$$

where r is the length of the internuclear vector \mathbf{r} , and θ is the angle between \mathbf{r} and the magnetic field. In solid samples this results in coupling between one spin and all its neighbours, but in liquids and solutions rapid motion causes \mathbf{r} , and thus θ , to fluctuate, so that \mathcal{H}_D is replaced by its isotropic average, which is zero. For this reason dipolar coupling has little direct effect in liquid state spectra (it cannot be entirely neglected, as it is one of the main sources of spin relaxation). The scalar coupling is a correction to the dipolar coupling which arises from the Fermi contact interaction: valence electrons can interact with two or more nuclei and thus mediate an interaction between them. Like dipolar coupling scalar coupling is anisotropic, but its isotropic average is non-zero; thus the relatively small isotropic scalar coupling is the dominant spin–spin interaction in the liquid state.

Dipolar coupling is removed because isotropic tumbling reduces it to its isotropic average. If the motion is *anisotropic* then the average may become non-zero; this can occur if the anisotropy of the molecular magnetic susceptibility causes molecules to align slightly with the magnetic field, resulting in small residual dipolar couplings. The effect is largest when the magnetic susceptibility is high, and this approach has proved helpful in investigating proteins bound to oligonucleotides [104]. Larger alignments, and thus larger residual couplings, can be observed using liquid crystalline solvents or cosolvents [105], which align strongly in the magnetic field and then themselves act to order other dissolved molecules.

This approach has been used [106] to implement Grover’s quantum search on a two qubit NMR quantum computer based on chloroform dissolved in a liquid crys-

tal solvent. The effective Hamiltonian in this system is

$$\mathcal{H} = \omega_I I_z + \omega_S S_z + \pi(J_{IS} + 2D)2I_z S_z \quad (9)$$

where D is the residual dipolar coupling [106], allowing the gate rate to be increased by a factor of 8. It is not yet clear how generally useful this approach will be.

Two qubit gates in larger systems

The description above is not only confined to one and two qubit gates; it is in fact confined to such gates in two qubit computers. If these gates are to be used to build networks with three or more qubits it is necessary to consider how they will function in larger spin systems.

The situation for one qubit gates is relatively straightforward, as these can still be implemented using selective RF pulses (although the problem of frequency selection, discussed below, becomes more serious). For two qubit gates, however, a more detailed analysis is necessary. For a general n spin system, the Hamiltonian is

$$\mathcal{H} = \sum_i \omega_i I_z^i + \sum_{i < k} \pi J_{ik} 2I_z^i I_z^k, \quad (10)$$

including n Larmor frequency terms for each spin, and a total of $n(n-1)/2$ spin-spin coupling terms, connecting every pair of spins. In real systems some of the J_{ik} coupling constants will be so small that they can be neglected, but it is still useful to consider the most general case. Consider, for example, a system of three spins, conventionally called I , R and S ; in this case there will be three Larmor frequency terms, and three spin-spin couplings, J_{IR} , J_{IS} , and J_{RS} .

It is in principle relatively simple to implement gates using the direct method. Each transition is split into four (under the influence of two couplings); if selective excitation is applied at just one of these four frequencies this corresponds to a doubly controlled three qubit gate, such as the Toffoli gate. Alternatively by exciting two transitions two qubit gates, such as controlled-NOT, can be achieved. In practice in large spin systems it will become difficult to pick out the right set of transition frequencies, and it is likely that some transitions will overlap.

The more common approach is to use Hamiltonian sculpting to convert equation (10) into the desired form. Clearly this requires refocusing the $n-2$ additional Larmor frequency terms, as well as the $(n-1)(n-2)/2$ extra spin-spin couplings. This can be achieved using spin echoes [82, 88]. Unfortunately it is not possible to use just a single echo to refocus all the interactions; instead it is necessary to consider how the echo sequences interact with one another. The simplest method is to nest spin echoes applied to each spin within one another, but this naïve approach requires an exponentially large number of refocusing pulses. Fortunately this problem

can be sidestepped by using efficient refocusing sequences [88, 107], which allow refocusing to be achieved with a quadratic overhead.

It is rare to find a large spin system where all the couplings have significant size. Coupling is a fairly local effect and so large coupling constants are only found between spins that are fairly close within the spin system; thus the coupling network is described by a non-complete graph [88]. This greatly simplifies the problem: not only does it reduce the number of couplings which have to be refocused, but it also simplifies the echo patterns needed to refocus the Larmor frequencies [85, 88]. Thus the overhead required for refocusing echoes is greatly reduced.

It might seem that it would not be possible to implement all the desired logic gates in such a spin system, as some of the requisite spin-spin couplings are missing. In fact this is not a problem, as long as every pair of spins is connected by some chain of couplings. Quantum SWAP gates [80, 83] can be used to move quantum information along this chain; the overhead imposed by these SWAP gates is at worst linear in the size of the spin system. In most cases the advantages of using a partially coupled spin system significantly outweigh the disadvantages.

Multiqubit gates

As described above, NMR techniques can be used to implement conventional one and two qubit gates, and thus any desired quantum network. This approach, imitating existing theoretical models of quantum computers, was adopted by all the early papers on NMR quantum computation. It is not clear, however, that this is the best approach: it might be more sensible to consider what types of gates NMR systems are good at providing, and then seeing whether these are valuable in quantum computation. To take a simple example the natural two qubit gate for NMR systems is the controlled phase shift, not the controlled-NOT gate, and in many quantum algorithms phase shifts are exactly what is needed. For example, NMR quantum computers can readily implement Grover's quantum search without using an ancilla qubit to convert oracle calls into phase shifts [14, 15, 16].

A more complex, but more interesting, example is the implementation of multiqubit gates. As the NMR Hamiltonian, equation (10), contains terms connecting multiple pairs of qubits, it should be possible to use this Hamiltonian to build certain multiqubit gates directly. This was briefly discussed above, when considering the direct implementation of Toffoli gates in a multi-spin system, but Hamiltonian sculpting should allow the approach to be used more widely. To date this idea has received only brief analysis [87], but this is likely to be a productive source of gates in the next few years.

The problem of selective excitation

From the descriptions above it might seem that implementing quantum logic gates in NMR quantum computers is essentially solved, and that the solutions scale fairly well. This is almost, but not quite, true as one major problem remains: selective excitation.

All the techniques described above rest on the assumption that it is possible to address individual qubits, so that interactions can be refocused. For NMR quantum computation (or indeed any NMR pulse sequence) this is achieved using frequency selection, rather than more conventional spatial localisation techniques, and this approach is only possible if the NMR transitions all have well separated frequencies; in particular it is simplest if the separation between any pair of Larmor frequencies is much greater than the width of the NMR multiplets, that is the sum of the spin-spin couplings. Note that in contrast with conventional NMR experiments it is not sufficient simply to selectively excite one spin; it is also essential that other spins remain *completely* unaffected.

With small spin systems this is fairly easy to achieve, but with larger systems it can become quite difficult. For example, the range of Larmor frequencies found for ^1H nuclei in simple organic compounds, and working at a ^1H frequency of about 500 MHz is only about 5000 Hz, and this limited frequency range can soon “fill up”. Increasing the number of spins not only increases the number of NMR multiplets, but also increases the width of each multiplet by introducing more spin-spin couplings. With other nuclei the situation is similar, although usually less serious (the ^1H frequency range is unusually narrow).

A partial solution is provided by turning to heteronuclear spin systems. As the NMR frequencies of different nuclei are very different, it is trivial to achieve nucleus selective, and thus spin selective, excitation. The comparative simplicity of heteronuclear NMR quantum computation explains its early, and enduring, popularity. Unfortunately this approach can not be continued indefinitely, as the number of suitable nuclei is small, the obvious candidates being ^1H , ^{13}C , ^{15}N , ^{19}F and ^{31}P .

It seems likely that the problem of selective excitation will prove a serious difficulty in constructing large NMR quantum computers. Although it is difficult to assess exactly what the limit will be, it is notable that the largest number of spins of one nuclear type used to date is six ^1H nuclei [85]; one other paper has described computations involving four ^{13}C nuclei and three ^1H nuclei [39], while all other authors have used at most three spins of any one nuclear type. Assuming that it is practical to address six spins of each of the five nuclei listed above, this suggests a limit of around 30 qubits imposed by the problem of selective excitation. Actually designing and synthesising such a spin system is another problem entirely.

DECOHERENCE

In order to perform large quantum computations it is essential that errors be kept under control. In practice this means that the decoherence time must be very long in comparison with the gate time, although methods of error correction (see section) allow this criterion to be slightly relaxed. The situation for NMR quantum computation might appear extremely good, as systems with very long relaxation times are known: for example, the spin-lattice relaxation time (T_1) of ^{129}Xe can be thousands of seconds [108]. As scalar spin-spin coupling constants can reach hundreds of Hertz, and dipolar couplings can be even larger, a naïve calculation suggests that it should be possible to implement about 10^4 – 10^6 gates before decoherence becomes a serious problem.

In fact this calculation is meaningless for two reasons. First, these extremely long relaxation times are always spin-lattice relaxation times; the spin-spin relaxation times (T_2), which provide a better measure of the decoherence rate, are much shorter (typically below ten seconds). Secondly, the relaxation times and gate rates are taken from different spin systems, and it is not possible to simultaneously achieve them in a single molecule. The long relaxation times observed for ^{129}Xe gas arise precisely because Xe gas atoms have only weak interactions with their neighbours, and such systems are of little apparent use for quantum computation as they provide no mechanism for logic gates. As the scalar coupling is related to an underlying dipolar coupling, and dipolar coupling is one of the two principal sources of relaxation in spin- $\frac{1}{2}$ nuclei, spin systems suitable for constructing NMR quantum computers inevitably possess shorter relaxation times.

One further feature of decoherence in NMR quantum computation deserves consideration. As NMR systems are ensemble quantum computers, the effect of decoherence is not simply to introduce errors, as occurs with more conventional designs. Rather these errors must be averaged over the ensemble, and if, as is often the case, these errors are fairly random in character, the overall effect is that the error terms will largely cancel out. Thus the principal effect of decoherence is to reduce the apparent signal strength. This is clearly visible in some quantum counting experiments [19, 109], where decoherence appears as an exponential decay in signal.

It is difficult to estimate a realistic limit to NMR quantum computation arising from decoherence; however, current experiments have been performed involving hundreds of logic gates [19, 109], and it seems likely that the limit is about one thousand gates.

QUANTUM ERROR CORRECTION

Quantum error correction, and its companion fault tolerant computation [110, 111, 112, 113, 114, 115], play a central role in considerations of the practicality of large quantum computers: while small quantum computers may handle errors fairly well the fragility of highly entangled states renders large quantum computations highly vulnerable. Error correction tackles this by diagnosing these errors and correcting them, while fault tolerant computation provides methods for minimizing the spread of errors, and in particular reducing the impact of errors in error correction schemes. Simple examples of such schemes have been implemented on NMR quantum computers [77, 84].

The importance of these techniques can hardly be overstated; until their discovery many authors believed that it would be completely impossible to build a large quantum computer as it would be hopelessly error prone. Unfortunately this benefit comes at a price: error correction involves a substantial overhead as each logical qubit must be encoded using many ancilla qubits. While this overhead has been substantially reduced by new codes [115] it is still at least an order of magnitude. More importantly, however, this assumes that it is possible to reuse ancilla qubits in order to repeatedly correct errors; in turn this requires the ability to reinitialize ancilla qubits at will. With current NMR quantum computers this cannot be achieved, and it is necessary to use a supply of fresh ancilla qubits at each stage. In this case the overhead becomes so large as to be completely impractical.

READ-OUT

Once a quantum computation has been performed it is necessary to use some read-out scheme in order to extract the result. As NMR quantum computation is implemented using an ensemble of spin systems, read-out involves ensemble measurements, and thus expectation values. This can have a number of profound consequences.

In simple cases NMR read-out is little different from more conventional schemes. Suppose that a quantum computation ends with the answer qubits in eigenstates. In this case it is only necessary to determine whether each qubit is in state $|0\rangle$ or $|1\rangle$, which is equivalent to determining the expectation value of σ_z . This can be achieved either by exciting the corresponding spin with an RF pulse and observing the phase of the NMR signal [10, 19], or by examining the multiplet structure in the NMR spectrum of a neighbouring spin, or by a combination of these techniques [13].

A more interesting situation occurs when the algorithm ends with one or more answer qubits in superposition states. A conventional quantum computer will return one of the corresponding answers at random, while an

ensemble quantum computer will return an ensemble average over the set of all possible answers [9, 19]. In most cases this result is not particularly useful, and it is necessary to recast the algorithm so that a single well defined result is obtained [9, 19]. In some special cases, however, ensemble measurements can be advantageous [19].

A similar situation arises when NMR techniques are used to implement phenomena such as quantum teleportation [79, 116]. Traditional teleportation schemes use strong measurements to project an unknown quantum state into the Bell basis; classical results from these measurements are then used to determine which of a set of unitary transformations must be used to finish the protocol. In NMR teleportation, however, such projective measurements and classical readout cannot be used. Instead it is necessary to use conditional evolution to perform the final unitary transformation [79].

This lack of projective measurements may also have consequences for quantum computation using a single pure qubit [64, 65]. The model of Knill and Laflamme [64] assumes only ensemble measurements, and so accurately reflects the nature of NMR quantum computation, while the work of Parker and Plenio [65] assumes that projective measurements can be made. It remains to be seen how significant this difference actually is.

CONCLUSIONS

It is useful to draw some overall conclusions about the potential usefulness of liquid state NMR as a technique for implementing *large* quantum computers. For *small* quantum computers liquid state NMR techniques are well ahead of the competition: indeed in most areas of experimental quantum information processing there quite simply is no competition! However, there are several serious difficulties with extending this approach to large systems, and it seems unlikely that any very large liquid state NMR quantum computer will ever be built.

The issue most commonly raised is initialization: the pseudo-pure states used in NMR are far from pure, with typical polarizations below 10^{-4} , and, more seriously, an exponential fall off as the size of the computer is increased. This alone would appear to limit liquid state NMR quantum computers to about 30 qubits.

In fact this assessment is probably too pessimistic. There are many techniques for increasing signal strengths, and while none of them offer an immediate solution, several have potential. Furthermore, recent theoretical results suggest that pure states may be less important than previously believed. If low polarizations were the only difficulty preventing the construction of a large scale NMR quantum computer, then it seems highly likely that a solution would be found. Unfortunately there are other, more serious, problems.

Constructing quantum logic gates in small systems is

easy, indeed almost trivial; this simplicity explains the rapid initial progress in NMR quantum computation. Early concerns about a potential exponential increase in the complexity of implementing these gates have proved unfounded, with the discovery of methods for implementing two qubit gates in multi-spin systems with (at worst) quadratic overhead. Little thought has, however, been paid to the problem of selective excitation and the crowding of frequency space; in my personal opinion this is likely to be the first serious barrier to building NMR quantum computers with many more than ten qubits.

The problem of decoherence is, of course, common to all potential implementations of quantum computers. The relatively long decoherence times of nuclear spins, which appear to make them good candidates as qubits, arise because they interact only weakly with their environment. Unfortunately these weak interactions are also manifested as low gate rates, and so the ratio of decoherence time to gate time is not as large as one might hope. Nevertheless NMR decoherence processes are fairly well behaved, and are not likely to prove an insuperable problem in systems of ten qubits.

The difficulty of performing practical quantum error correction schemes, arising from the lack of selective reinitialization, is a serious problem for building *large* quantum computers; this, however, is only likely to become an issue if all other difficulties are solved.

The inability to perform projective measurements, and the difficulty of dealing with ensemble averaged data, is probably not a serious problem in its own right. This property makes it difficult to use NMR experiments to test fundamental questions in quantum mechanics, but has few major implications for computation. Indeed in some cases, such as when considering the effects of decoherence, it can actually be an advantage. Unlike some other issues, however, this limitations appears to be inherent in the liquid state NMR experiment, and it is not at all clear how it can be bypassed.

Finally, it is interesting to compare current liquid state NMR quantum computers with Kane's radically different, but ultimately related, proposal for a solid state NMR quantum computer [33]. It is notable that Kane's proposal keeps many of the advantages of NMR, but also manages to tackle some of the most serious difficulties described above. Firstly, Kane's proposal uses external "gates" to modulate both the Larmor frequencies and the spin-spin coupling constants of nuclei. This should remove all the difficulties with implementing quantum logic gates. Secondly, the proposal includes a scheme for making projective measurements on single spins, thus also providing a simple initialization scheme.

Even if, as seems likely, a large liquid state NMR quantum computer is never built, quantum computation will still owe much to NMR. By providing the first working quantum computers, no matter how small, NMR has reinvigorated the field. Tricks long known to NMR

spectroscopists are now being applied in NMR quantum computations, and many of these will have applications in other technologies. NMR quantum computation has had, and still has, much to offer.

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